Femtosecond "snapshots "of gap–forming charge-density-wave correlations in quasi-two-dimensional dichalcogenides $1T$-TaS_2 and $2H$-$TaSe_2$.

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Time-resolved optical spectroscopy of collective and single-particle excitations of $1T$-TaS_2 and $2H$-$TaSe_2$ reveals the presence of a large gap in the excitation spectrum on the femtosecond timescale, associated with the formation of various degrees of CDW order. In common with superconducting cuprates, excitations with energies less than the full gap show much slower relaxation. This separation of timescales cannot be explained in a quasi-2D Fermi-Liquid picture with an anisotropic gap but rather suggests the formation of a fluctuating spatially inhomogeneous state eventually forming a long-range ordered state at low temperatures.

Dimensionality can have quite a profound effect on the ground state properties of materials. For example quasi-one-dimensional metals often undergo a Peierls-distortion to become insulating at low temperatures[1], or form strange "Luttinger" metals in which collective excitations give rise to peculiar low-temperature properties[2]. The ground state of two-dimensional (2D) materials in some cases is also very peculiar. Quasi-2D charge-density wave (CDW) dichalcogenides have been receiving renewed attention recently, particularly because they are thought to exhibit some important similarities to the high-temperature superconducting cuprates (HTSC). Both are layered, highly anisotropic materials which are often described in terms of a quasi-2D Fermi surface (FS) in their normal state. In HTSCs, it is commonly believed that the superconducting gap has nodes along certain directions on the FS due to the d-wave component of the order parameter, whereas in 2D-CDW systems a CDW gap is also expected only along certain wavevectors, remaining gapless (and metallic) on other regions of the FS. The low-energy single particle excitations in the two classes of compounds might therefore be expected to show some important common features related to reduced dimensionality. However, the validity of the Fermi-liquid (FL) concept when applied to low-temperature properties in HTSCs has repeatedly been brought into question, suggesting that new insight into the physics of quasi-2D systems may be gained by investigating the low-energy electronic gap structure and carrier recombination dynamics of quasi-2D CDW dichalcogenides with femtosecond spectroscopy. The time-resolved technique has been shown to give femtosecond "snapshots" of the low-energy gap structure and as such presents an excellent alternative viewpoint compared to the more usual time-averaging frequency-domain spectroscopies[3, 4, 5].

Here we apply the technique to the study of single-particle (SP) and collective excitations in two different quasi-2D CDW dichalcogenides $1T$-TaS_2 and $2H$-$TaSe_2$. We focus on the issue of single particle dynamics and gap formation in the two materials (note that the effective shutter speed is on the femtosecond timescale) and compare the results with the predictions based on a quasi-2D FL picture, finding some fundamental discrepancies between the expected behaviour and our observations.

Both $1T$-TaS_2 and $2H$-$TaSe_2$ exhibit a series of successive phase transitions, starting from a highly anisotropic quasi-2D metallic state at high temperatures, and ending with a commensurate (c-) CDW state at low temperatures [6]. (A summary of the sequence of transitions is shown in the inserts to Fig.1.) At room temperature $1T$-TaS_2 is in a nearly-commensurate (nc-) CDW phase (Fig.1a). Around $T_{nc-c} = 200$ K it undergoes a strongly first-order "lock-in" transition to a c-CDW state [6]. In spite of the expected appearance of a gap in parts of the Fermi surface due to nesting at T_{nc-c}, the whole FS was found to exhibit a "pseudogap" feature already at room temperature with a finite density of states (DOS) at E_F [7]. Upon lowering the temperature, a further *abrupt* decrease in the DOS is observed near E_F at T_{nc-c}, accompanied by an order of magnitude *increase* in resistivity. Yet in spite of the presence of a CDW gap at low temperatures $1T$-TaS_2 is reported to have a small but finite DOS at E_F in the low-temperature c-phase [7].

$2H$-$TaSe_2$ on the other hand is expected to bear close resemblance to cuprates. It exhibits metallic properties above room temperature (Fig.1b). Upon cooling it undergoes a second order phase transition to an incommensurate (i-) CDW state at $T_{n-i} = 122$ K. This phase transition is reportedly accompanied by the appearance of a gap on the Fermi surface (FS) centered at the K point, but apparently - according to photoemission studies[8] - remains gapless on the part of the FS centered at the Γ point. The transition is accompanied by a decrease in the scattering rate and a corresponding *drop* in resistivity [9]. The onset of a c-CDW phase at $T_{i-c} = 88K$ leaves the excitation spectrum as well as the transport and thermodynamic properties almost unaffected [6, 8]. Upon warming from the c-phase, an additional "striped" incommensurate (si-) phase has been reported between 92 and 112 K [10].

The experiments reported here were performed on freshly cleaved single crystals, using a pump-probe set-up with a mode-locked Ti:Sapphire laser (50 fs pulses at 800 nm) for both pump and probe pulse trains. The photoin-

duced change in reflectivity $\Delta\mathcal{R}/\mathcal{R}$ was measured using a photodiode and lock-in detection. The pump laser power was kept below 5 mW and the pump/probe intensity ratio was ∼100. The steady-state heating effects were accounted for as described in [11] giving an uncertainty in temperature of < 2 K. As the optical penetration depth is $\gtrsim 100$ nm, the technique is essentially a *bulk* probe, and since we are using very weak photoexcitation [3] the system as a whole remains close to equilibrium.

The sequence of relaxation events after photoexcitation is common to metals (incl. superconductors) and CDW materials [3, 12, 13]: the photoexcited (PE) carriers first rapidly thermalize by *e-e* scattering (within $\tau_{e-e} \approx 10$ fs) and then transfer their energy to the lattice with a characteristic electron-phonon relaxation time given by $\tau_{e-ph} = k_B T_e/\hbar(\lambda\langle\omega^2\rangle)$ [12, 13], where λ is the electron-phonon coupling constant, and $\langle\omega^2\rangle$ is the mean square phonon energy. Using $\omega \approx 200$ cm^{-1} [14] and $\lambda \approx 0.3$ [15] we obtain (for the excitation intensities used here) $\tau_{e-ph} \approx 100$ fs which is the time required for the PE carriers to relax to energies close to E_F. If a gap in the DOS is present near E_F, the resulting relaxation bottleneck causes carriers to accumulate in states above the gap. The population of these carriers $n(T,t)$ can then be probed by a delayed probe laser pulse and its time evolution directly gives the *energy* relaxation time τ_s for their recombination. From the T-dependence of $n(T,t)$ direct information on the gap magnitude, its T-dependence, as well as something about its anisotropy can be extracted [3]. In addition to this SP response, the perturbation of the charge density caused by the PE carriers can excite CDW collective modes[5, 16] - particularly the amplitude mode (AM) - which can be observed as an oscillatory response superimposed on the SP relaxation data.

In Fig.1 we show the induced reflectivity $\Delta\mathcal{R}/\mathcal{R}$ in $1T$-TaS_2 and $2H$-$TaSe_2$ as a function of time after photoexcitation at different temperatures. The general feature of the data in both cases is the appearance of a decaying transient and a superimposed oscillatory response due to the SP and collective mode relaxations respectively. The two contributions can be easily deconvolved [5] by fitting the transient reflectivity signal to a function of the form:

$$\Delta\mathcal{R}(t,T)/\mathcal{R} = A(T)e^{-t/\tau_A}\cos(\omega_A t + \phi_0) + S(T)e^{-(t/\tau_s)^s} + D(T). \quad (1)$$

The first term describes the modulation of the reflectivity due to coherent oscillations of the AM mode of frequency ω_A, where $\Gamma_A = \pi/\tau_A$ is the AM damping constant [16]. The second term describes the SP response and the third term describes the "background" which is the contribution from decay components with lifetimes longer than the inter-pulse separation of 10 ns [4]. The signal appeared to be independent of probe polarization in both materials.

Let us first analyze the oscillatory AM response. In $1T$-TaS_2 (Fig. 1a)) below T_{c-nc}, the frequency of oscillation corresponds closely to the AM frequency ω_A as determined by Raman spectroscopy. The T-dependence of ω_A and Γ_A determined from the fit are plotted in Fig. 2a) showing excellent agreement with the established Raman data [14]. Γ_A strongly increases near T_{c-nc}. A profound hysteresis is observed in the T-dependence, where a rather sharp drop in ω_A (and increase in Γ_A) coincides with T_{c-nc} - see inset to Fig. 1a). In contrast, for $2H$-$TaSe_2$ the T-dependence of ω_A and Γ_A (Fig. 2b)) is much more mean-field like, becoming overdamped ($\omega_A \simeq \Gamma_A$) around $T = 110$ K. (For comparison, Raman data for ω_A and Γ_A is also shown [14].)

Let us now turn to the SP excitations. While in $2H$-$TaSe_2$ the SP transient can be reproduced well by a *single* exponential decay over the whole temperature range (i.e. $s = 1$), the SP relaxation dynamics in $1T$-TaS_2 requires a *stretch* exponential decay fit with $s \sim 0.5$ to fit the data adequately. (Although the SP transient in $1T$-$TaSe_2$ can also be fit by the sum of two exponentials, the two components have the same T-dependence, which suggests that we are dealing with a single relaxation process with non-exponential dynamics rather than two distinctly independent processes). The observation of a stretch exponential decay - which typically describes systems with a spread of relaxation times - is consistent with the observed finite DOS at E_F below T_{c-nc} [7]. (Since $\tau \sim 1/\Delta$ [Ref. 3] the observed stretch exponential decay actually implies a near-Gaussian spread of $1/\Delta$.)

The T-dependences of the amplitude $S(T)$ and τ_s (using $s = 0.5$) for $1T$-TaS_2 and $2H$-$TaSe_2$ are plotted in Figs. 3a) and b) respectively. In $1T$-TaS_2 the relaxation dynamics are clearly strongly affected by the lock-in transition around 200K. We observe an abrupt hysteretic change of $S(T)$ and τ_s around T_{nc-c}, consistent with an abrupt appearance of a gap at T_{nc-c} suggested by other experiments [7]. Upon further cooling S remains more or less constant, while τ_s slowly decreases. Upon warming, a rapid drop in S and τ_s associated with gap closure now occurs at around 220 K, consistent with the hysteresis observed in the collective mode response in Fig. 2a). Above 230 K the photoinduced transient is fast and very weak.

The single-exponential fit to the SP relaxation in $2H$-$TaSe_2$ over the entire T-range is surprising, since below T_{n-i}, the system is expected to have a highly anisotropic gap with gapless regions over parts the FS[8] implying that the relaxation should deviate strongly from a single exponential. (A similar problem arises in cuprates, where the decay is also exponential, in spite of the fact that nodes in the gap would expected to give rise to strongly non-exponential decay[3].) The T-dependence of $S(T)$ and relaxation time τ_s obtained from the single exponential fit to the data on $2H$-$TaSe_2$ are plotted in Fig. 3. Below ~ 120 K both $S(T)$ and $\tau_s(T)$ can be very well described by model for carrier relaxation across a well-defined temperature-dependent gap. The theoretical fit for $S(T)$ and $\tau_s \propto 1/\Delta(T)$ using the model by Kabanov et al. [3] using a BCS gap function is superim-

posed. The value of the gap from the fit $2\Delta(0) = 70 \pm 10$ meV is somewhat smaller than the maximum gap obtained from tunneling [17], but in good agreement with the maximum gap value of 65 meV from ARPES[8]. The divergence of τ_s and the drop in $S(T)$ as $T \rightarrow T_{i-n} \approx 120$ K from below are unmistakable signs of a T-dependent gap which is closing near T_{i-n} [3]. Above ~ 140 K the relaxation time and $S(T)$ show only a weak T-dependence with $\tau_s \sim 0.1 - 0.17$ ps, close to the estimated τ_{e-ph}. τ_{e-ph} is expected to increase with increasing temperature (see Fig. 3 d) and laser power [12], which is indeed observed: at room temperature a $\sim$30 % increase in τ_s is observed at a 3-fold increase in the pump fluence - apparently confirming that the relaxation above $T \sim 140$ K is primarily due to $e - ph$ thermalization [13]. On the other hand, the behavior of $S(T)$ just above T_{i-n} is rather unusual, showing a rapid increase with increasing temperature between 120 and ~ 140 K. This could be attributed to the presence of segments of ordered CDW [5] giving rise to a negative $\Delta R/R$ transient[18] with vanishing amplitude at $T \gg T_{i-n}$ in addition to positive transient due to $e - ph$ thermalization. Since the two relaxation times are comparable, adding up the two would result in the behavior just as observed in Fig. 3b. It should be noted that similar behavior was found also in $K_{0.3}MoO_3$ [5].

A very important feature of the data is the slow relaxation component $D(T)$ shown in Fig. 3e) for $2H$-$TaSe_2$. This relaxation is typically attributed to intragap localized states near E_F and its T-dependence gives independent data on the the T-dependence of the gap [4]. The magnitude of D is very small and more or less T-independent in $1T$-TaS_2, but is very pronounced in $2H$-$TaSe_2$ with a T-dependence typical for a T-dependent gap[4]. Comparing with cuprates, the behaviour of $2H$-$TaSe_2$ is similar to overdoped $YBa_2Cu_3O_{7-\delta}$[19]. The model in ref. [4] predicts $D(T)$ to be proportional to $\Delta(T)^{-3/2}$ at low temperatures (regardless of the gap anisotropy) which is in good agreement with the observed T-dependence of the fast SP lifetime τ_s, amplitude $S(T)$ as well as $\nu(T)$. A fit to the data using $\Delta(T)$ of BCS form is shown as a solid line in Fig. 3e) for $2H$-$TaSe_2$.

The emerging picture based on the time-domain measurements on 2H-$TaSe_2$ presented here is one in which the low-temperature state shows *a clear large gap* in the excitation spectrum on the femtosecond timescales (not just a depression in the DOS such as is observed in time-averaged experiments). There is also clear evidence for very slow relaxation of excitations whose energy is less than the maximum gap. The observed behaviour is in clear contradiction with a FL interpretation, where the SP relaxation would be expected to occur primarily in the gapless regions of the FS (in the nodes for the case of superconductors). The observation of only a large SP gap on the femtosecond timescale implies that there are certain momenta associated with the gapless regions which are either inaccessible to quasiparticles, or - implying a breakdown of the FL picture alltogether - simply that *extended* states with these wavevectors do not exist at all. The latter behaviour is consistent with the notion of fluctuating *locally ordered* regions in space, in which case it becomes clear why one cannot speak of FL-like quasiparticle excitations with well defined momenta. The precursor "pseudogap state" appears to be associated with the fluctuating presence of fully gapped short-range-ordered CDW patches or segments, similar to the locally gapped regions in real space arising from a statistically fluctuating population of pre-formed pairs in HTSCs[3, 19]. We can also remark on the striking similarity in the SP relaxation dynamics - and gap structure - between $2H$-$TaSe_2$ below T_{n-i}, and overdoped and optimally doped HTSC[19] below T_c. In both cases the SP relaxation dynamics is governed by the opening of a mean-field-like gap, characteristic of a 2^{nd} order phase transition below T_{n-i} (or T_c). The observed divergence of the relaxation time and T–dependence of $S(T)$ are unmistakeable signatures of such a gap indicating that *a collective* mechanism is responsible for joining the short-range local correlated segments into a long-range ordered CDW (or superconducting) state. This behaviour is quite different to the more glass-like $1T$-TaS_2 with its 1^{st} order behaviour and stretch exponential relaxation.

These time-resolved experiments show that irrespective of the fundamental underlying cause for the instability, these quasi-2D materials, in common with HTSCs show a transition from a high-temperature uniform metallic state to a low-temperature correlated state via the formation of a dynamically inhomogeneous intermediate state in which local precursor CDW segments (or pairs in the case of HTSCs) appear on the femtosecond timescale. The time-averaged response (such as is observed in ARPES or infrared spectra) may then be thought of as the superposition of the different components in the inhomogeneous state, while the observed anisotropy reveals the directionallity of the interaction which leads to the formation of long range order.

Figure 1. The transient reflection $\Delta R/R$ from a) $1T$-TaS_2 and b) $2H$-$TaSe_2$ at a number of temperatures above and below T_{nc-c} and T_{n-i} respectively. The signals are offset for clarity. Insets: The phase diagrams of bulk $1T$-TaS_2 and $2H$-$TaSe_2$.

Figure 2. The amplitude mode frequency ν_A (full circles) and damping constant $\Gamma_A = 1/(\pi\tau_A)$ (open circles) as a function of temperature for a) 1T-TaS_2 and b) $2H$-$TaSe_2$. The squares represent the Raman data [14]. ν_A and Γ_A show hysteresis near T_{c-nc} in $1T$-TaS_2, shown on an expanded T-scale in the inset to panel a).

Figure 3. The T-dependence of fast component amplitude, $S(T)$, for a) 1T-TaS_2 and b) $2H$-$TaSe_2$. In panels c) and d) the T-dependences of the corresponding relaxation times (a stretch exponential was used in case of $1T$-TaS_2). Open symbols: data taken upon warming, solid symbols: data taken upon cooling. e) The T-dependence of the slow component amplitude. Solid lines in b), d) and e) are fits to the data - see text.

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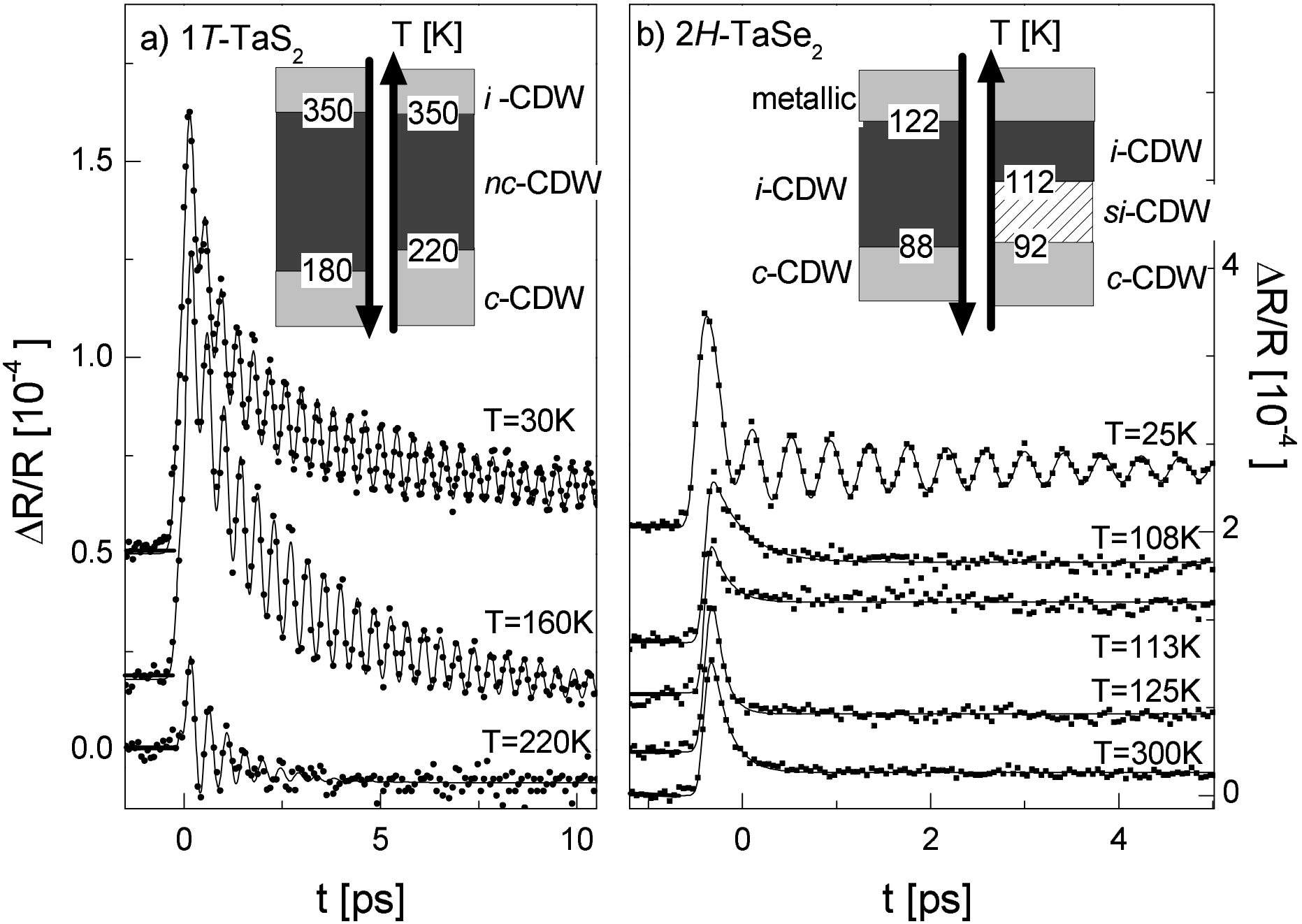
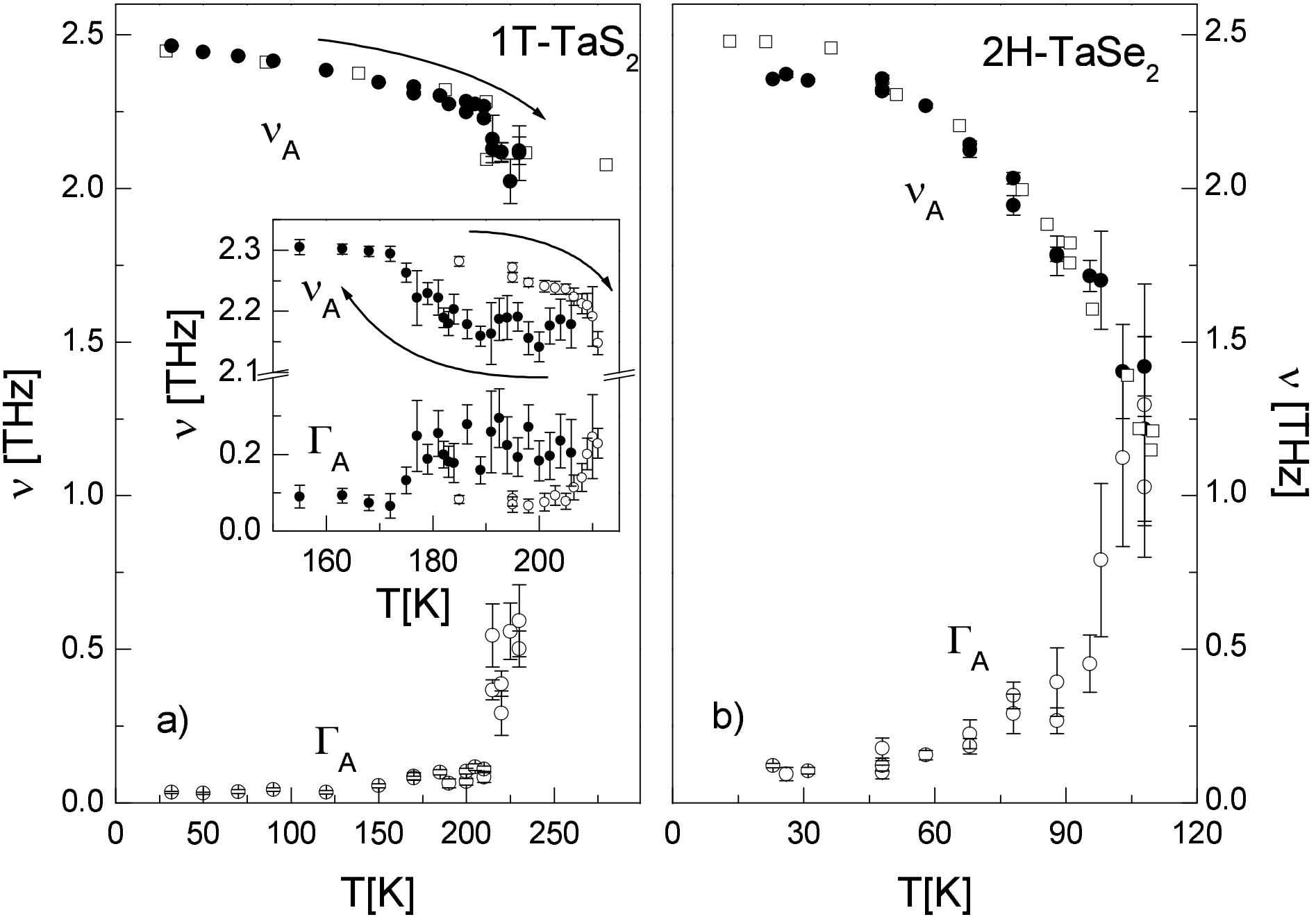
Demsar et al., Fig.1



Demsar et al., Fig.2



Demsar et al., Fig.3